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Synthesis of SAN-PB-SAN Triblock Copolymers via a "Living" Copolymerization with Macro-Photoiniferters

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ABSTRACT: A technique is described for the synthesis of poly((styrene-*co*-acrylonitrile)-*block*-butadiene-*block*-(styrene-*co*-acrylonitrile)) (SAN-PB-SAN) triblock copolymers through polybutadiene-based photoiniferters. Dihydroxy- and dicarboxy-terminated polybutadienes were transformed into the chloro-terminated compounds, which were subsequently reacted with sodium diethyldithiocarbamate into macro-photoiniferters. The dicarboxy-terminated polybutadiene was found to produce unstable dithiocarbamate end groups because of loss of CS_2. The dihydroxy-terminated polybutadiene (M_n = 3300 g/mol) was successfully transformed into a macro-photoiniferter, which was used as a photoinitiator for the "living" copolymerization of styrene/acrylonitrile mixtures to obtain the title compounds. By variation of the polymerization time and macroiniferter concentration, the vinyl sequence length and composition of the triblock copolymers could be regulated. The macroiniferters and block copolymers were characterized by GPC, elemental analysis, and ^{1}H NMR.

Introduction

It is well-known that block or graft copolymers, containing blocks of the same chemical structure as the heterophases in an incompatible binary polymer blends, are capable of compatibilizing these polymer mixtures.[1−4] When localized at the interface between the immiscible blend components, the block copolymers lower the interfacial tension, thereby dispersing the polymer blend into smaller domains due to stabilization of the particles. Consequently, the blends show improved ductility, because of enhanced force transfer between the different phases.

Previously, we reported the synthesis of segmented PB(PS-*block*-PB)$_n$, PB(SAN-*block*-PB)$_n$,[5] and PB(SMA-*block*-PB)$_n$[6] block copolymers by thermal (co)polymerization of the required monomers with a synthesized thermal polybutadiene-based iniferter. These block copolymers are novel potential compatibilizing agents for various different blends. The segmented PB(SAN-*block*-PB)$_n$ block copolymers, developed by us, proved to be very efficient compatibilizers for low-density polyethylene (LDPE)/poly(vinyl chloride) (PVC) blends,[7] already giving a pronounced improvement in mechanical properties and morphology of the blend at compatibilizer concentrations of 1% or less. Because styrene-*co*-acrylonitrile (SAN) copolymers are known to be miscible with a variety of homopolymers, such as poly(methyl methacrylate),[8−11] poly(carbonate),[12,13] poly(vinyl chloride),[14] and poly(ϵ-caprolactone)[15] (within a certain composition range of the SAN copolymer), the developed segmented PB(SAN-*block*-PB)$_n$ block copolymers, when hydrogenated, are potential compatibilizers for blends of polyolefins with all of the above mentioned polymers.

The architecture of a block copolymer is of extreme importance for its compatibilizing effectiveness. The number of blocks appear to play a significant role here. Both theoretically and experimentally, a lot of research has been done on this subject, leading to extremely different and contradictory conclusions. For example, in a theoretical analysis by Noolandi,[16] it is argued that, because of its structure, less (AB)$_n$ multiblock copolymer than AB diblock copolymer is lost in bulk phases as micelles and mesophases. Also, he argues that a diblock copolymer is oriented perpendicularly to the interface plane while a multiblock copolymer will lie in the plane of the interface. Therefore, a multiblock copolymer molecule would cover a larger part of the interfacial surface than a diblock copolymer. This prediction is in agreement with results of recent computer simulations by Balazs,[17−20] who compared the compatibilizing effectiveness of various copolymers with different architectures. According to these simulations the determining factor for the improvement in interfacial adhesion is the number of effective crossings or "stitches" which a block copolymer chain is able to form across the interface. Therefore an increasing number of alternating A and B blocks in the block copolymer at a polymer/polymer interface will give an increase in interfacial adhesion, provided that the blocks are long enough to be able to form entanglements with the bulk polymers, thereby reducing the risk of chain pull-out. On the other hand, in various experimental studies quite different effects have been reported. For example, in a paper by Teyssié et al. diblock copolymers have been found to be more efficient compatibilizers than triblock copolymers,[21] while in some other papers quite the opposite effect is presented,[22−24] and another one states that there is no difference in compatibilizing effectiveness between di- and triblock copolymers.[25] So, obviously the effect of compatibilizer architecture is still rather questionable.

To study the effect of the number of blocks in this new type of SAN-PB block copolymer on their compatibilizing behavior, we searched for a way to make di- or triblock copolymers of the same type. Most block copolymers are produced by anionic techniques. However, anionic polymerization is hardly suitable for the synthesis of random copolymers. We applied a so-called photoiniferter technique, providing a "living" radical polymerization, for the preparation of SAN-PB-SAN block copolymers, since the easiest and most effective way of synthesizing random copolymers is by free radical polymerization. The term "iniferter" was introduced by Otsu to describe free radical initiators with simultaneous chain transfer and terminating proper-

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ties.[26−30] Among various other compounds, he investigated the photoinitiating behavior of tetraalkylthiuram disulfides, which he reported to initiate photopolymerizations with a living character due to the triple function of these iniferters. He showed that when these compounds are used in photovinyl polymerizations, the resulting polymers are always end capped at both ends with the iniferter fragments. So, by irradiation of the dithiocarbamate-terminated polymer in the presence of a new monomer, the polymerization could be restarted, providing a block copolymer.

Recently, Roha et al. reported a photoiniferter method for the synthesis of graft copolymers.[31−33] They prepared various graft polymers by the substitution of chlorinated substituent containing polymers with thio groups and subsequent grafting reactions by photopolymerization of monomers with the thio-substituted polymers. We adapted this method for the synthesis of SAN-PB-SAN triblock copolymers, by synthesis of a macro-photoiniferter based on polybutadiene (PB) and subsequent photocopolymerization of the required comonomers, using the synthesized polybutadiene-based macro-photoiniferter (MI) as the initiating species.

Experimental Section

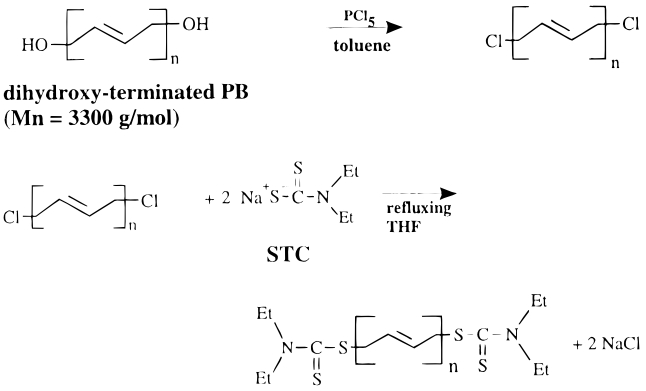
Materials. Phosphorus pentachloride, hydroxy-terminated polybutadiene (Aldrich), and carboxy-terminated polybutadiene (Scientific Polymer Products, Inc.) were used as received. Sodium diethyldithiocarbamate (Aldrich) was recrystallized from methanol before use. Toluene was distilled from sodium/benzophenone. Tetrahydrofuran was purified by distillation from $LiAlH_4$. Styrene and acrylonitrile were purified by vacuum distillation from finely powdered CaH_2 and were used within 24 h after purification.

Synthesis of Macroiniferter MI-3300 Based on Dihydroxypolybutadiene (M_n 3300). Dihydroxy-terminated (1.9 OH groups per chain) polybutadiene (PB) (27.4 g; 8.32 mmol) was dissolved in 150 mL of dry toluene and dried by distilling off 50 mL of toluene azeotropically. After the mixture was cooled down to room temperature, a 3.53 g quantity of phosphorus pentachloride (16.6 mmol) was added to the solution. The system was stirred overnight. The polymer solution was precipitated in cold methanol (−50 °C). The resulting chloro-terminated polybutadiene was dried in vacuum. Conversion: 93% (elemental analysis Cl).

The obtained chloro-terminated polybutadiene was dissolved in 200 mL of tetrahydrofuran under N_2 atmosphere in a three-necked flask. After addition of a 2-fold molar excess of sodium diethyldithiocarbamate to the solution, the system was heated to reflux and kept reacting at that temperature overnight. During the reaction, sodium chloride precipitated as a side product. The solution was cooled, filtered, and subsequently precipitated into cold methanol (−50 °C). The polymer was dried in vacuum at 40 °C. The number of diethyldithiocarbamate end groups per chain was found to be 1.68 (elemental analysis N and S), giving a total end group conversion of 88%.

Synthesis of SAN-PB-SAN Triblock Copolymers. In a typical experiment, a 0.50 g (0.14 mmol) quantity of MI-3300 was placed in a small Pyrex flask under nitrogen atmosphere. Subsequently, 7.5 g (72.0 mmol) of freshly distilled styrene as well as 1.0 g (18.8 mmol) of freshly distilled acrylonitrile was added and the mixture was stirred magnetically until the polybutadiene macroiniferter had dissolved in the comonomer mixture. The ampule was placed at a distance of 2 cm from a hand-held 365 nm UV lamp. The lamp was water cooled to avoid heating of the polymerization mixture. The photopolymerizations were carried out at room temperature. After the required polymerization time the mixture was dissolved in tetrahydrofuran and precipitated directly into methanol at room temperature. After a second precipitation from tetrahydrofuran into hexane to remove the remaining nonreacted polybutadiene, the obtained block copolymer was filtered and dried in vacuum.

Scheme 1. Synthesis of a Macro-Photoiniferter Based on a Dihydroxy-Terminated Polybutadiene (M_n = 3300)



Reaction of Acetyl Chloride with Sodium Diethyldithiocarbamate. Sodium diethyldithiocarbamate (1.75 g; 10.2 mmol) was dissolved in 50 mL of freshly distilled tetrahydrofuran under nitrogen atmosphere. Acetyl chloride (1.20 g; 15.3 mmol) was added slowly via a syringe. During the reaction, the color of the solution turned from colorless to deep yellow and a significant amount of salt precipitated. A part of the product was isolated by filtration of the solution and subsequent evaporation of the solvent, after which the product was analyzed by ^1H NMR. After 2 days, a new NMR analysis of the crude product was performed. The solution was not clear any more and had lost the deep yellow color by then.

Analyses. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer. Molecular weights of the polymers were determined by GPC with a refractive index detector using THF as eluent and PS standards for calibration.

Results and Discussion

In this study macro-photoiniferters (MI) were synthesized from a dihydroxy-terminated polybutadiene (M_n = 3300, D = 1.90) and a dicarboxy-terminated polybutadiene (M_n =10200, D = 1.65). Both polybutadienes contained approximately 20% of 1,2 butadiene units. MI-3300 was used to initiate the photo-copolymerization of styrene and acrylonitrile, resulting in SAN-PB-SAN triblock copolymers.

Synthesis and Characterization of MI-3300. The synthesis of MI-3300 is presented schematically in Scheme 1. The hydroxyl end groups of the polybutadiene were first converted into chlorine groups using phosphorus pentachloride. This step was found to proceed almost quantitatively (93%) by elemental analysis of chlorine. Also, ^1H NMR spectra showed that the small peaks of the CH_2OH end groups (4.05−4.23 ppm) of the starting material (Figure 1a) had disappeared after the chlorination step. In the NMR spectrum of the chlorine-terminated product in $CDCl_3$, two small doublets at 4.0 and 3.75 ppm owing to the CH_2Cl end groups of respectively a terminal 1,4-butadiene and a 1,2-butadiene unit can be seen (Figure 1b). Relative intensities give a calculated chorine functionality of the polybutadiene of 1.79, which corresponds to a conversion of approximately 90%. This is in good agreement with the conversion calculated by elemental analysis. Moreover, it was confirmed with ^1H NMR that no double bonds were chlorinated using this procedure. This was done by looking at the CH/CH_2 ratio of the polybutadiene before and after chlorination, which remained unchanged. After purification of the chlorine-terminated polymer by precipitation into cold methanol (−50 °C), it was reacted with sodium diethyldithiocarbamate (STC) in refluxing tetrahydrofuran for 20 h. During this

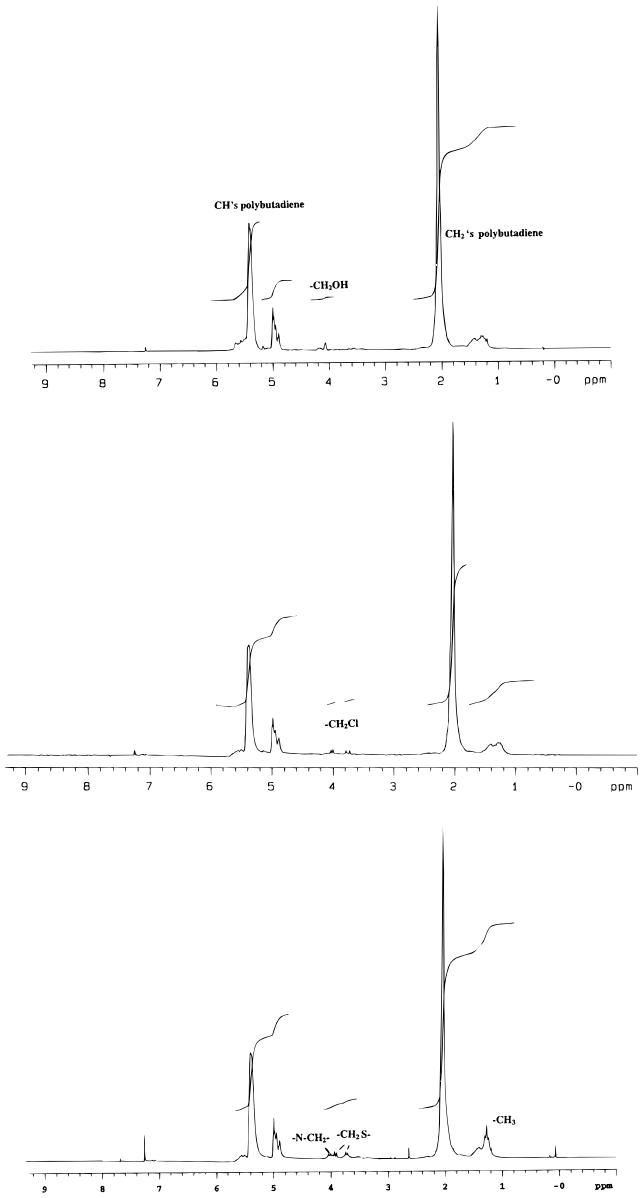


Figure 1. (a) Top: ^{1}H NMR spectrum of a hydroxy-terminated polybutadiene. (b) Middle: ^{1}H NMR spectrum of the same polybutadiene after the chlorination step. (c) Bottom: ^{1}H NMR spectrum of MI-3300.

reaction sodium chloride precipitated as a side product, which was removed by filtering the solution after the reaction. Elemental analysis of sulfur in the product indicated a diethyldithiocarbamate end functionality of 1.68 (see Table 1), while the nitrogen content of the polymer indicated complete conversion, which could mean that part of the iniferter end groups had decomposed into amine end groups by loss of carbon disulfide. Also, the chlorine content of the macro-photoiniferter was checked to be sure that no polybutadiene double bonds were chlorinated by formed HCl during the first reaction step. Elemental analysis of the product showed that the material contained no chlorine.

The ^{1}H NMR spectrum of the polymeric iniferter in $CDCl_3$ showed small resonance signals, owing to the $-CH_3$ groups (1.25 ppm) and CH_2 groups (3.7−4.1 ppm) of the dithiocarbamate end groups (Figure 1c). The signals of the CH_2 groups are very small, and therefore, they are difficult to characterize. However, we think they consist of a quartet at 4.0 ppm, owing to the $-NCH_2-$ group of the dithiocarbamate end group as well as two doublets at 3.9 and 3.75 ppm, owing to the $-CH_2S-$ groups of respectively a terminal 1,4-butadiene and a 1,2-butadiene unit. Integration leads to a iniferter end functionality end of 1.98. However, this is a very rough estimation.

Unfortunately, the triplet at 1.25 ppm owing to the CH_3 end groups coincides with one of the polybutadiene CH_2 signals and therefore determination by integration is rather hazardous. By use of the polybutadiene CH/CH_2 ratio found for the starting material, we could calculate an end functionality of 1.71 on the basis of the CH_3 groups, which is surprisingly close to the value obtained by elemental analysis. However, in this case, NMR cannot be regarded as an accurate instrument for the determination of the iniferter end functionality of the polybutadiene.

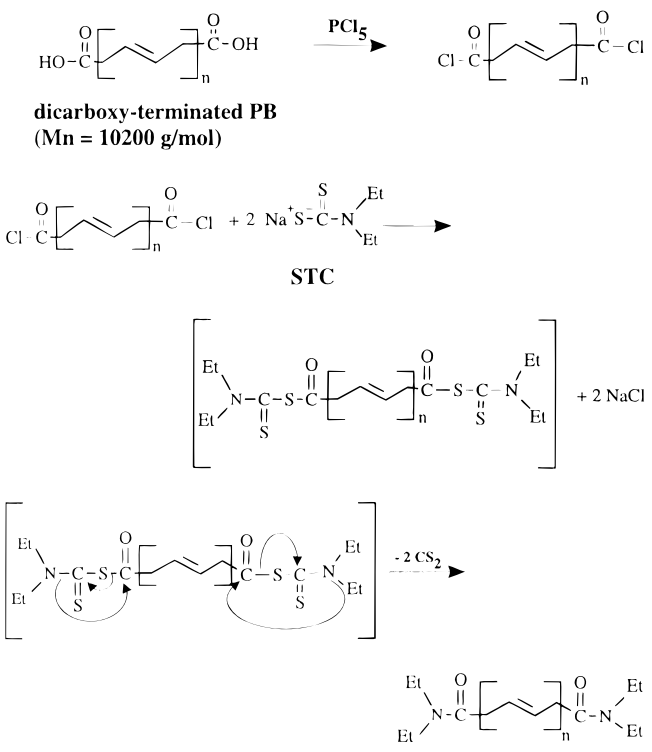
Synthesis and Characterization of MI-10200. The synthesis of the photoiniferter based on the higher molecular weight dicarboxy-terminated polybutadiene proved to be more complicated. After the synthesis was performed, as described above, elemental analysis of the product showed a nitrogen content as would be anticipated, while only a very small trace of sulfur was found in the material (Table 1). Because of the higher molecular weight of the polybutadiene, and thus a lower concentration of end groups, NMR analysis of the end groups could not provide a clear explanation for this absence of sulfur in the product. However, we suspected the formed iniferter end groups to be thermally unstable because of the carbonyl group present. This decomposition by loss of carbon disulfide and formation of an amide end group, as depicted in Scheme 2, would explain the absence of sulfur in the material. To verify this assumption, a small-scale reaction of acetyl chloride (CH_3COCl) with STC was carried out in THF and analyzed by ^{1}H NMR. Figure 2a shows the ^{1}H NMR spectrum of the crude product directly after the reaction was stopped. The spectrum shows that the thioester has indeed been formed (signals A−C) but is already decomposing into *N*,*N*-diethylacetamide by loss of carbon disulfide. The ^{1}H NMR spectrum of the product after a couple of days (Figure 2b) shows that the thermally unstable thioester has decomposed completely into the corresponding amide. A further indication that indeed *N*,*N*-diethylacetamide has been formed is the fact that the two CH_2 groups E and G and the two CH_3 groups F and H, from the ethyl groups attached to the nitrogen atom, no longer form one quartet and one triplet, as was seen for the thioester. The two CH_2 groups now give a sextet (3.15−3.35 ppm) of intensity 1:3:4:4:3:1, formed by two different quartets, of which the outer two signals coincide. The two CH_3 groups now give a quintet (1.0−1.15 ppm) of intensity 1:2:2:2:1, which is formed by two triplets, of which the outer signals coincide. This behavior is typical for N,N-disubstituted amides (e.g. dimethylformamide) and can be explained by the limited rotation around the C(O)−N linkage because of its partial double-bond character, causing a chemically different environment for the two N-substituents.

Because of the proven unstability of this type of thioester, we are confident that the same decomposition process had occurred with the thioester-terminated polybutadiene. Therefore, this synthesis method is not suitable for the synthesis of MI-10200. In this work we used the prepared macroiniferter MI-3300 as an initiator for the photocopolymerizations of styrene/acrylonitrile.

Table 1. Characteristics of Synthesized Macroiniferters

macroiniferter code	prepolymer	M_n of prepolymer	elemental anal. of MI N (%) calc	N (%) found	S (%) calc	S (%) found	iniferter end functionality
MI-10200	$PB(COOH)_2$	10200	0.30	0.36	1.22	0.07	
MI-3300	$PB(OH)_2$	3300	0.78	0.79	3.60	3.02	1.68

Scheme 2. Proposed Decomposition of a Macro-Photoiniferter Based on a dicarboxy-Terminated Polybutadiene (M_n = 10 200)



Synthesis and Characterization of SAN-PB-SAN Triblock Copolymers, Prepared by Photoinitiated Copolymerization of Styrene and Acrylonitrile with MI-3300. While disulfides such as TMTD (tetramethylthiuram disulfide) initiate polymerizations by both thermal and photo mechanisms, monosulfide compounds like substituted dithiocarbamate or xanthate groups are initiated only by means of UV irradiation at normal temperatures. Therefore it was necessary to perform the copolymerizations of styrene and acrylonitrile by a photoinitiated mechanism. Photopolymerizations with this type of dithiocarbamate-terminated polymers are predicted to proceed by a "living" radical mechanism.[26−30] Because of the relative stability and high chain transfer constant of the dithiocarbamate radicals, which are produced during photoinitiation, they function as counterradicals for the propagating polymer radicals, thereby avoiding termination steps like bimolecular recombination or hydrogen abstraction. Therefore, this type of copolymerization can be considered as a continuous insertion of acrylonitrile and styrene between the propagating polymer radical and the dithiocarbamate counterradical. The "living" character of this type of copolymerization should provide block copolymers with different SAN block lengths by variation of the polymerization time.

By using the PB-photoiniferter MI-3300 as an initiator for the free radical copolymerization of styrene and acrylonitrile, SAN-PB-SAN triblock copolymers could be obtained (Scheme 3). Characteristics of the copolymerizations initiated by MI-3300 and the resulting triblock

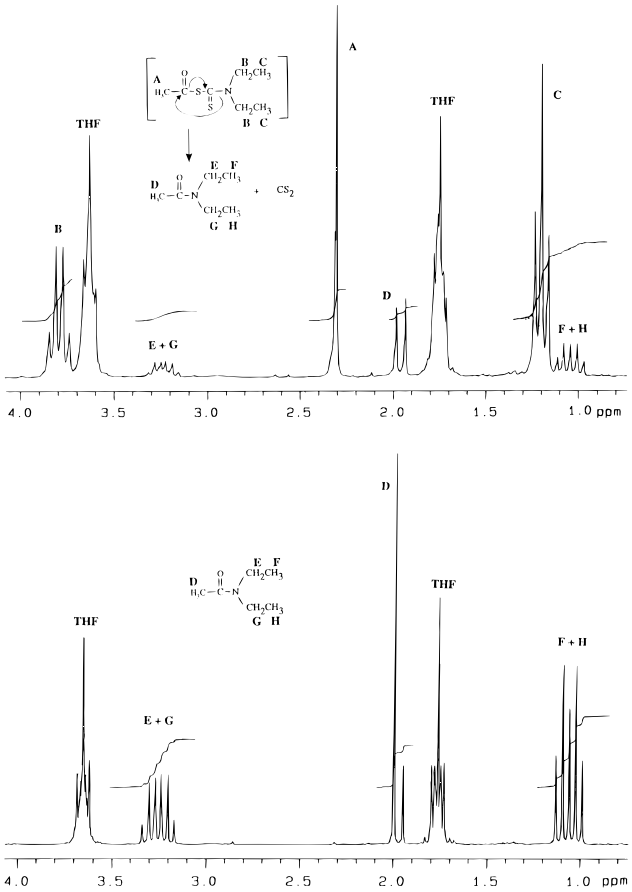
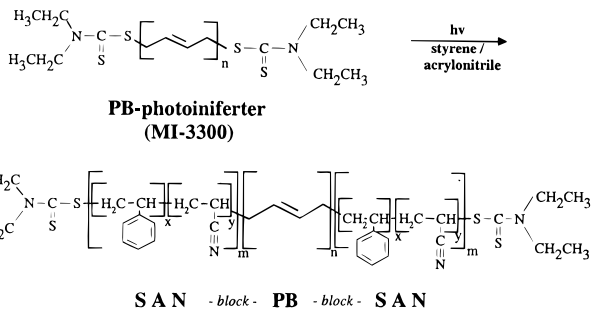


Figure 2. (a) Top: ^{1}H NMR spectrum of a reaction mixture of acetyl chloride and STC, showing formation of the thioester and partial decomposition of the product into *N*,*N*-diethylacetamide. (b) Bottom: ^{1}H NMR spectrum of the same reaction mixture as shown in Figure 1a after 2 days, showing complete decomposition of the product into *N*,*N*-diethylacetamide.

Scheme 3. Synthesis of SAN-PB-SAN Triblock Copolymers by Copolymerization of Styrene and Acrylonitrile with MI-3300



copolymers are given in Table 2. In all cases the polymerization time was 16 h, while both the macroiniferter concentration and the monomer feed composition were varied. The overall compositions of the block copolymers were determined by combination of NMR and elemental analysis. First the butadiene/styrene ratio in the material was determined by ^{1}H NMR. By combination of these results with the acrylonitrile

Table 2. Characteristics of Photocopolymerizations of Styrene/Acrylonitrile with MI-3300

$[MI]_{eff}$ (mmol/L)[a]	f_{AN} in monomer feed (mol %)	F_{AN} in SAN mol %[b]	F_{AN} in SAN wt %[b]	consumption of MI-3300 (wt %)	conversion of SAN (wt %)	wt % of SAN in block copolymer	M_n of block copolymer (10^4 g/mol) NMR[c]	M_n of block copolymer (10^4 g/mol) GPC	SAN block length (10^3 g/mol)
46.4	30.7	33.3	20.3	n.d.	n.d.	92.2	4.2	3.9	17.7
48.3	24.0	29.0	17.2	79.7	77.8	89.5	3.2	3.7	16.7
50.4	18.3	24.2	14.0	n.d.	n.d.	89.1	3.0	3.2	14.2
85.2	22.5	31.5	19.0	85.5	46.2	73.2	1.3	2.0	8.2
98.5	21.4	29.9	18.0	63.6	54.4	78.6	1.6	1.9	7.7
154.3	24.8	32.9	20.0	69.2	40.3	62.3	0.9	1.2	4.2
163.3	26.0	44.4	28.9	78.4	37.3	55.5	0.8	1.1	3.7
182.0	21.6	34.3	21.0	73.2	41.4	57.1	0.8	1.2	4.2

[a] Effective concentration of iniferter groups from MI-3300. [b] From % N in block copolymer determined by elemental analysis, corrected for % N from iniferter groups. [c] Calculated from block copolymer composition, assuming exclusive formation of triblock copolymer.

content of the block copolymer, which was calculated from the nitrogen content determined with elemental analysis, the overall composition could be calculated. The nitrogen contents, which were obtained from elemental analysis, were corrected for the nitrogen atoms originating from the diethyldithiocarbamate end groups. The obtained block copolymer compositions were used to make a theoretical prediction of the molecular weight of the block copolymers. As can be seen from Table 2, these predicted molecular weights are reasonably consistent with the molecular weights determined by GPC. This is an indication that predominantly triblock copolymer has been formed. Furthermore, GPC showed no additional peak of nonreacted polybutadiene homopolymer, which has apparently been removed by the two-step precipitation procedure. Also, the formation of diblock copolymer could not be confirmed by GPC. This would surely have given rise to an additional peak in the GPC, or at least a peak shoulder, its molecular weight being almost half of that of the triblock copolymer.

An increase of the macroiniferter concentration in the polymerization system has been found to give rise to a lower monomer conversion and molecular weight and of the corresponding triblock copolymers (see Table 2). When the polybutadiene macroiniferter truly gives rise to a "living" copolymerization, the number average polymerization degree of the SAN blocks in the block copolymer at 100% monomer conversion should be equal to the ratio of (co)monomer concentration and the concentration of "living" ends of the polybutadiene iniferter. Therefore we performed some calculations to check if this is indeed the case. We assumed that the number of "living" ends present in the polymerization system is equal to the part of the polybutadiene iniferter which had been consumed during polymerization, multiplied by two, which is the number of dithiocarbamate end groups per polybutadiene chain:

$$[LE] = 2([MI\text{-}3300]_0)(Cons./100) \qquad (1)$$

Here [LE] represents the concentration of "living" ends in the system, $[MI\text{-}3300]_0$ represents themacroiniferter concentration at start of polymerization, and Cons. represents the macroiniferter consumption in weight percent.

The number average polymerization degree, extrapolated to 100% monomer conversion, was calculated as follows:

Table 3. Comparison of Average Polymerization Degree at Total Monomer Conversion to $[M_1 + M_2]_0/[LE]$

[LE] (mmol/L)	$[M_1 + M_2]_0$ (mol/L)	$[M_1 + M_2]_0/[LE]$	$P_{n(100)}$
45.8	10.28	224.4	240.3
74.6	10.11	135.5	150.9
86.7	10.18	117.4	113.6
126.7	10.33	81.5	89.5
152.4	10.41	68.3	112.3
158.5	10.13	63.9	89.0

$$P_{n(100)} = \frac{M_n(SAN)}{xM_{(AN)} + (1-x)M_{(St)}} \frac{100}{C} = \frac{M_n(SAN)}{104.15 - 51.09x} \frac{100}{C} \qquad (2)$$

Here $P_{n(100)}$ designates the number average polymerization degree, extrapolated to 100% monomer conversion, $M_n(SAN)$ denotes the number average molecular weight of SAN blocks in the triblock copolymer, x is the acrylonitrile content of the SAN blocks in mole percent, $M_{(AN)}$ and $M_{(St)}$ represent the molecular weight of acrylonitrile (53.06 g/mol) and styrene (104.15 g/mol), respectively, and finally C is the monomer conversion in weight percent. In Table 3 the results of the calculations are presented. The calculated number average degree of polymerization of the SAN blocks at 100% monomer conversion seems to be reasonably consistent with the monomer/"living" end ratio. Only at high ratios of monomer concentration to "living" end concentration a rather large difference exists. Because at these high [M]/[LE] ratios monomer conversions are relatively low, the error in molecular weight determined by GPC will give a much larger error for the values obtained after extrapolation to 100% monomer conversion, because of the factor $100/C$ in eq 2. However, in general it is possible to synthesize block copolymers with the required SAN block lengths by choosing the right monomer/iniferter ratio. Because of the expected "living" character of these photopolymerizations, another way of controlling the block copolymer composition should be by varying the polymerization time.

Time Dependence of SAN Copolymerizations with MI-3300. To study the "living" character of the photocopolymerization of styrene and acrylonitrile with MI-3300, we took samples at various polymerization times and analyzed them by GPC, ^{1}H NMR, and elemental analysis. In Table 4 the characteristics of this copolymerization are presented. Every 1.5 h a sample was extracted from the reaction mixture during the first 7.5 h of polymerization. Finally, the copolymerization was stopped completely after 16 h. Before sample extraction, the UV lamp was turned off. It was switched on again immediately after sample extraction had taken place. Despite this procedure, which leads to recombi-

Table 4. Time Dependence for Photocopolymerizations with MI-3300

$t_{pol.}$ (h)	consumption of MI (wt %)[a]	conversion of SAN (wt %)[a]	SAN content of block copolymers (wt %)[b]	M_n of block copolymer (10^3 g/mol) NMR[c]	M_n of block copolymer (10^3 g/mol) GPC	M_w/M_n of block copolymer	M_n of SAN blocks (10^3 g/mol)[c] NMR	M_n of SAN blocks (10^3 g/mol)[c] GPC	iniferter end functionality of block copolymer[d]	AN content of SAN blocks (wt %)[e]
1.5	51.6	2.2	50.2	6.9	11.1	5.1	1.7	3.7	1.76	18.6
3.0	59.2	4.5	68.3	10.7	12.6	2.7	3.6	4.6	1.59	19.8
4.5	52.4	9.0	82.9	20.0	20.4	2.1	8.0	8.5	1.62	17.9
6.0	84.3	17.2	85.2	22.6	22.3	2.4	9.5	9.4	1.60	18.4
7.5	87.1	19.5	86.4	24.4	25.0	2.7	10.5	10.8	1.44	18.8
16.0	72.2	40.2	94.0	55.3	61.5	2.7	25.9	29.0	1.49	17.4

[a] Calculated from block copolymer composition and block copolymer yield. [b] Calculated from NMR data. [c] Assuming exclusive formation of triblock copolymer. [d] From sulfur content block copolymers, determined by elemental analysis. [e] From nitrogen content, determined by elemental analysis, corrected for nitrogen atoms from end groups.

nation of the propagating polymer radicals with the thiocarbamate radicals, there is a continuous progress in SAN conversion and molecular weight during the copolymerization. This is a clear indication that this type of copolymerization can be terminated and subsequently restarted at any given point during polymerization, which means that there must be a "living" mechanism involved. The molecular weight of the triblock copolymers and their SAN blocks, calculated from the block copolymer composition determined by NMR, was found to be in good agreement with the molecular weights determined by GPC (Table 4).

Table 4 shows that macroiniferter consumption continues to increase until approximately 4.5 h. After this period it stabilizes at a value of approximately 80 wt %, which is near the value which would be anticipated from the end group functionality (1.68) of the macroiniferter. Because of the continuous initiations of new chains during the initial stage of copolymerization, the polydispersity of the block copolymers is fairly high in this polymerization stage. It decreases to a minimum of 2.1 after this period and then rises somewhat to 2.7 after 16 h. Because of the slow (i.e. rate determining) radical-producing step in this type of radical polymerization using dithiocarbamates, leading to a slow slow initiation as well as a slow equilibrium between active and dormant polymer radical sites, this method does not allow the production of polymers having polydispersities comparable to those attainable by use of anionic polymerization.

A "living" type of polymerization should show a linear increase in both monomer conversion and molecular weight of the corresponding polymer with polymerization time. This rule indeed applies for the SAN copolymerization with the polybutadiene photoiniferter, as can be seen in Figure 3. Also, when the molecular weight of the SAN blocks in the block copolymer is plotted against monomer conversion, a linear dependence is found (Figure 4). So, the part of the macroiniferter which initiates the copolymerization truly provides a "living" polymerization mechanism.

To investigate whether the number of dithiocarbamate end groups of the triblock copolymers change during the copolymerization with MI-3300, their sulfur content was determined by elemental analysis. In combination with their number average molecular weight, determined by GPC, the average number of end groups of the triblock copolymers could be calculated. It appears that there is only a slight decrease in number of end groups during the course of copolymerization from 1.68 dithiocarbamate end groups per chain for the macroiniferter to 1.49 end groups for the finally obtained block copolymer after 16 h of polymerization (see Figure 5). This would imply there is a small extent of termination

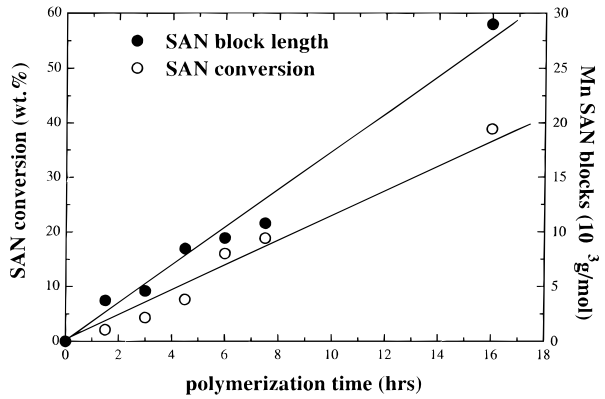


Figure 3. Time dependence of SAN block length and conversion during copolymerization of styrene and acrylonitrile with MI-3300.

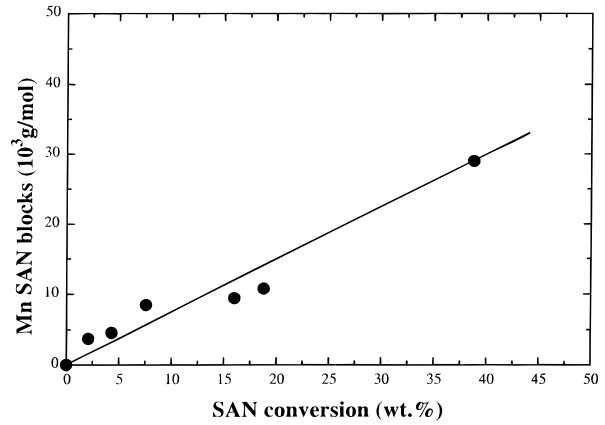


Figure 4. Development of SAN block length with SAN conversion for copolymerization of styrene and acrylonitrile with MI-3300.

reactions by disproportionation or reinitiation by some of the dithiocarbamate counterradicals. However, this is not in line with the observed "living" character of the SAN copolymerization with MI-3300. Of course, the determination of block copolymer end groups by elemental analysis is quite risky because of the very low sulfur content of the block copolymer (<1 wt %), especially for higher molecular weight block copolymers obtained at higher conversions. In combination with the error margin arising from the molecular weight determination by GPC, the observed decrease of dithiocarbamate end functionality of the block copolymers might well be an *artifact*. Anyhow, the vast majority of block copolymer chains remains end functional during the studied period of polymerization and thus continues to be capable of reinitiation, as observed by conversion and molecular weight measurements.

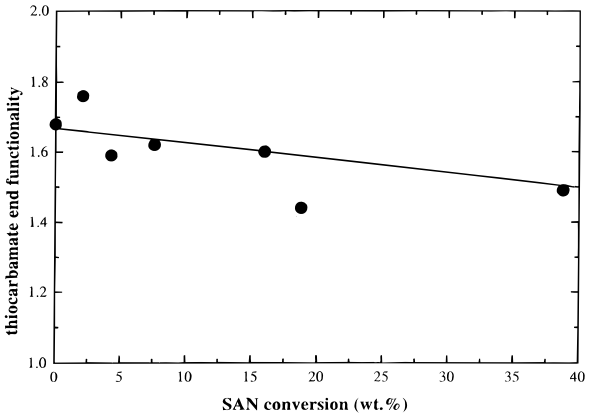


Figure 5. Decrease of the number of diethyldithiocarbamate end groups of block copolymer during copolymerization of styrene and acrylonitrile with MI-3300.

Finally, during the studied period of copolymerization the composition of the SAN blocks remains more or less at the same level (see Table 4), so propably there is no extensive composition drift and the insertion of the comonomers occurs in a fairly random manner. Therefore, it may be concluded that the presented "living" copolymerization is a well controllable method to prepare SAN-PB-SAN triblock copolymers.

Conclusions

We succeeded in synthesizing SAN-PB-SAN triblock copolymers by a macro-photoiniferter technique. Compositions and SAN block lengths in the triblock copolymers could be regulated by varying the macroiniferter concentration or polymerization time. Only the hydroxy-terminated polybutadiene was found to produce the desired macroiniferter (MI-3300), while the carboxy-terminated polybutadiene yielded an unstable thioester-terminated intermediate, which decomposed into the corresponding amide by splitting off carbon disulfide. Investigation of the time dependence of the copolymerization of styrene/acrylonitrile, using MI-3300 as a photoiniferter, showed a linear increase in SAN conversion and molecular weight during copolymerization, indicating a "living" mechanism for this type of copolymerization. The novel triblock copolymers reported here appear to be promising for use as compatibilizers for various blends. This is currently being studied and will be reported in the near future.

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